

Influence of vegetation in mitigation of methyl parathion runoff[☆]

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Vegetated wetlands are three times more effective at mitigating methyl parathion runoff than are non-vegetated wetlands.

Abstract

A pesticide runoff event was simulated on two 10 m × 50 m constructed wetlands (one non-vegetated, one vegetated) to evaluate the fate of methyl parathion (MeP) (PennCap-M[®]). Water, sediment, and plant samples were collected at five sites downstream of the inflow for 120 d. Semi-permeable membrane devices (SPMDs) were deployed at each wetland outflow to determine exiting pesticide load. MeP was detected in water at all locations of the non-vegetated wetland (50 m), 30 min post-exposure. MeP was detected 20 m from the vegetated wetland inflow 30 min post-exposure, while after 10 d it was detected only at 10 m. MeP was measured only in SPMDs deployed in non-vegetated wetland cells, suggesting detectable levels were not present near the vegetated wetland outflow. Furthermore, mass balance calculations indicated vegetated wetlands were more effective in reducing aqueous loadings of MeP introduced into the wetland systems. This demonstrates the importance of vegetation as sorption sites for pesticides in constructed wetlands.

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1. Introduction

Wetlands serve as transitional zones or “ecotones” between terrestrial and aquatic systems (Mitsch and Gosselink, 1993). They have several physical, chemical, and biological

uptake and degradative processes useful for treatment of point and non-point source pollution. Since the early 20th century, wetland losses attributed to agriculture have been dramatic. Extensive wetland draining in the 1960s and 1970s led to increased available agricultural production acreage. With this increased acreage, however, was a decrease in water quality enhancement capabilities of these former wetland areas. When rivers, streams, and lakes adjacent to the former wetland areas receive runoff following rainfall events, an increased potential for damage to water resources, such as increased sedimentation or fish kills, may occur. Even sub-lethal concentrations of potential agricultural contaminants may affect growth, reproduction, behavior, physiology, and long-term survival of aquatic flora and fauna (Anderson and Zeeman, 1995; Rice et al., 1997). In response to historic wetland losses, the US Department of Agriculture Natural Resource Conservation Service (USDA NRCS) has established four conservation

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practice standards (Codes 656, 657, 658, and 659) relating to constructed wetlands (USDA NRCS, 2002). By establishing these standards, farmers and other agricultural landowners are given instructions on how to develop and use constructed wetlands as a best management practice (BMP) to minimize non-point source pollution of water bodies.

Methyl parathion (*O,O*-dimethyl *O*-4-nitrophenol phosphorothioate) (MeP) was applied to US agricultural land in an amount excess of 270 000 kg active ingredient in 2002 (NASS, 2005). In Mississippi, MeP is the most intensively used pesticide, with a high water solubility (55 mg/L), $\log K_{ow}$ of 3.5, and K_{oc} of 5.1×10^3 (Coupe et al., 2000). Although not approved for urban use, MeP was detected in rain and air samples from both agricultural and urban sites in the Mississippi River Valley (Foreman et al., 2000). Majewski et al. (2000) consistently detected MeP in air samples along the Mississippi River from mid May–June through September.

The purpose of this study was to evaluate effectiveness of vegetated and non-vegetated wetlands in retaining MeP (PennCap-M[®]) during a simulated, worst-case scenario runoff event. From these data, the relative importance of aquatic vegetation versus no vegetation in facilitating the transfer or transformation of MeP was evaluated using mass balance calculations.

2. Materials and methods

2.1. Wetland exposure

Two constructed wetlands ($W = 11$ m; $L = 50$ m; $D = 0.2$ m) located at the University of Mississippi Field Station (Bay Springs, Mississippi, USA) were divided longitudinally, each into two replicate cells (5.5 m \times 50 m \times 0.2 m) using aluminum flashing (Fig. 1). Two cells contained two types of vegetation, *Juncus effusus* (256 ramets/m²) and *Leersia oryzoides* (43 ramets/m²). The remaining two cells were non-vegetated. Sampling sites for the study were established within each cell at 2.5, 5, 10, 20 m, and 40 m. Background water, sediment, and plant samples were collected at multiple locations within each wetland (one month prior to test initiation), with no detectable MeP measured.

A storm runoff event was simulated within the wetland systems in July 2000. Prior to amendment, basic water quality data were obtained for the vegetated and non-vegetated wetlands (Table 1). StowAway Tidbit temperature loggers (Onset Computers, Bourne, MA) were deployed in the water of each wetland during initial 10 d of the study. Initial MeP concentrations were based on recommended label application rates (0.42 kg active ingredient per ha). Suspended sediment, water, and MeP were mixed in a 110 L polyethylene mixing chamber prior to entering a 7.6 cm diameter PVC pipe for delivery. A mixture of MeP (0.24 kg active ingredient per liter), water, and suspended sediment (400 mg/L) was pumped into each cell simulating a 1% pesticide and water runoff from a 0.64 cm storm event across a 20 ha contributing area. The simulated runoff event took a total of 30 min to deliver at a rate of 530 L/min.

2.2. Wetland sampling

One liter amber glass bottles were used to collect grab samples of water at 30 min, 3 h, 6 h, 24 h, 96 h, 10 d, 27 d, 41 d, 64 d, and 182 d. Following collection, water samples were iced and transported to the USDA-ARS National Sedimentation Laboratory (USDA-ARS NSL) Oxford, MS, USA, for immediate extraction. Additionally, semi-permeable membrane devices (SPMDs supplied by EST, Kansas City, MO) were deployed ($n = 2$ per cell) for the first 96 h at the outflow (50 m) sites of each wetland cell. Sediment and plant samples were collected with all water samples, with the exception of the 6 h sampling period (water only), wrapped in aluminum foil, placed on ice for

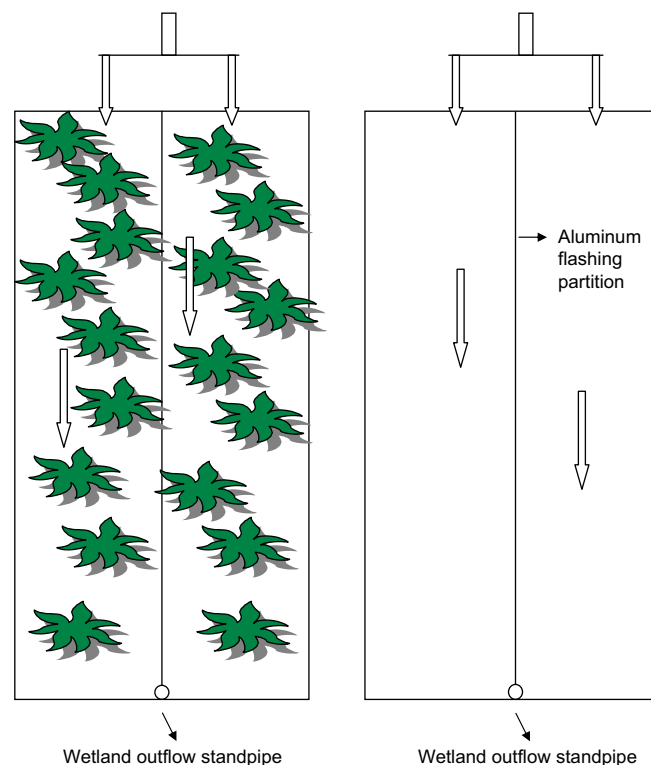


Fig. 1. Schematic of constructed wetlands at the University of Mississippi Field Station, Bay Springs, Mississippi, USA.

transport, and immediately stored in a freezer (-10 °C) upon arrival at USDA-ARS NSL until being dried for analysis. Using solvent-rinsed stainless steel spatulas, sediment samples were obtained from the top 1 cm, while plant materials were collected with solvent-rinsed scissors. Only that plant material exposed in the water column (between sediment and water surface) was collected for analysis.

2.3. Sample extraction and analysis

Water, plant and sediment samples were extracted using methods described by Bennett et al. (2000) and Moore et al. (2001). Briefly, aqueous samples were extracted with ethyl acetate using a liquid–liquid extraction method, while sediment and plants were extracted using ultrasonication with ethyl acetate. Silica gel cleanup was performed on water, sediment and plant extracts prior to final analysis. SPMDs were extracted using methods described by Bennett et al. (1996). Each SPMD was dialysed in a beaker containing 400 mL of hexane, covered with foil and placed in the dark at approximately

Table 1

Mean (\pm standard error) water quality parameters for vegetated and non-vegetated wetland cells at the University of Mississippi, Abbeville, MS, USA ($n = 3$) prior to initiation of study and median, maximum and minimum water temperatures recorded over first 10 d of the study

Parameter	Vegetated	Non-vegetated
pH (standard units)	6.7 ± 0.058	6.9 ± 0.11
Dissolved oxygen (mg/L)	2.3 ± 0.57	6.6 ± 0.23
Temperature (°C)	25.2 ± 0.75	27.8 ± 0.29
Conductivity (μ S/cm)	116 ± 3.8	42.6 ± 2.0
Temperature (°C)		
Median	25.5	29.5
Maximum	29.0	36.5
Minimum	21.5	22.5

18 °C for 48 h. Subsequently, SPMDs were removed and the dialysates were passed through anhydrous sodium sulfate and rotary evaporated to a volume of about 1 mL. Extracts were subject to gel permeation chromatography to remove co-extracted triolein and polyethylene constituents followed by silica gel cleanup, as above, prior to analysis.

MeP was analyzed via gas chromatography-microelectron capture detection with an HP 6890 gas chromatograph equipped with a DB5 MS column. The oven temperature program was as follows: 75 °C held for 1 min, to 225 °C at a rate of 40 °C/min. Injector and detector temperatures were set to 250 °C and 325 °C, respectively. Ultra high purity helium, the carrier gas (nexAir, Memphis, TN, USA), was set to a constant flow of 1 mL/min and ultra high purity nitrogen, the makeup gas (Whatman Nitrogen Generator), was set at a constant makeup flow of 60 mL/min. A multilevel calibration procedure was implemented with standards updated every ninth sample. Limits of detection (LOD) for MeP in water, sediments, and plants were 0.1 ng/mL, 0.5 ng/g, and, 0.5 ng/g, respectively. Based on fortified samples, mean extraction efficiencies were >90% for water, sediments, and plants.

2.4. Data analysis

Mass balances were performed using data on water, plants, and sediments collected along transects of the 50 m vegetated wetland cells and water and sediment data collected from the non-vegetated wetland cells for each sample point in time (30 min, 3 h, 24 h, and 10 d). This enabled quantitative evaluation of chemical partitioning and losses that occurred over the study duration. The mass balance at a given time point was determined as follows:

$$m_{\text{total}(t)} = m_{\text{w}(0-50)} + m_{\text{p}(0-50)} + m_{\text{s}(0-50)} \quad (1)$$

where $m_{\text{w}(0-50)}$, $m_{\text{p}(0-50)}$ and $m_{\text{s}(0-50)}$ reflect the total chemical mass (g) in water, plants and sediments over the 50 m wetland length. Integration of chemical masses in water was performed according to the trapezoidal rule:

$$m_{\text{w}(0-50)} = \sum_{i=0}^{n-1} \left((V_{\text{w}(i+1)} - V_{\text{w}(i)}) \left(\frac{C_{\text{w}(i+1)} + C_{\text{w}(i)}}{2} \right) \right) \quad (2)$$

where the term $(V_{\text{w}(i+1)} - V_{\text{w}(i)})$ represents the volume of water (L) bounded by a given transect interval (i.e. 0–2.5 m, 2.5–5.0 m, 5.0–10 m, etc.) and is multiplied by the average water concentration (C_{w}) measured at the interval boundaries. Water volumes between transects were estimated using the mean water depth (0.20 m) multiplied by the surface area of the transect interval and by accounting for water displacement by plants (assuming 20% of water was displaced by plant biomass in each transect). The mass calculations for plants and sediments were similar to Eq. (2) except that concentrations were measured in units of mg/kg and the volume terms were replaced by bulk sediment mass (kg) or plant biomass (kg). In the former case, the wetland surface area (m^2) within a given interval was multiplied by a sediment depth of 0.01 m and converted to sediment mass by assuming a bulk sediment density of 1200 kg/m^3 . The average area plant biomass (10.8 kg/m^2) within a transect interval was multiplied by the wetland width and interval distance to arrive at a plant biomass (kg) estimate. Aqueous MeP chemical half-lives ($t_{1/2}$) were estimated as $\ln(2)/k_2$, where k_2 represents the first order clearance constant (d^{-1}) estimated from the data on mass balance declines with time. MeP half-lives were also derived using mass balances for individual media (water, plants and sediments).

Ordinary least-square linear regression analyses were used to fit curves to base 10 log-transformed MeP water concentrations (y) versus log-transformed distance downstream from the injection point (x) (Sokal and Rohlf, 1981) to determine wetland lengths required to decrease initial loadings by 0.1%. Semi-log functions were also fit to the data, but produced inferior fits. For simplicity, only the maximum concentrations observed at each sampling distance (within 3 h) were used in the analyses. Distance calculations were estimated using regression data from pooled data from the two vegetated cells and pooled data from the two non-vegetated cells.

3. Results

3.1. MeP concentrations in water

In vegetated wetlands, aqueous MeP concentrations decreased rapidly with distance (Table 2). For example, 3 h following the initiation of the runoff simulation, mean water concentrations ranged from $452 \text{ } \mu\text{g/L}$ at the 2.5 m sampling site to $8.15 \text{ } \mu\text{g/L}$ at 20 m downstream, while concentrations were below detection limits at the 40 m sampling site. A similar trend was observed throughout the study's first 4 d. By 10 d, MeP was only detected within the first 10 m of the wetland. In non-vegetated wetlands, MeP concentrations generally decreased with distance within the initial 6 h of the study, while concentrations between sites began to stabilize to similar concentrations after 1 d of the study (Table 2). MeP was detected at the 40 m sampling site throughout the study in non-vegetated wetlands. Overall, water concentrations measured in both vegetated and non-vegetated wetlands after 10 d were approximately 1% of MeP concentrations detected at the beginning in the study. Results from deployed SPMDs indicated that MeP was not detected at the outflow (50 m) of the vegetated wetland within 96 h of the study, while a mean SPMD/MeP ($n = 2$) concentration of $8.83 \text{ } \mu\text{g/g}$ was measured at the outflow of the non-vegetated wetland.

3.2. Fate of MeP

The total nominal mass of MeP added to each wetland system was 86 g (43 g into each replicate wetland mesocosm). Measured masses applied to the wetland cells were consistent with the nominal mass, where the mass of MeP added to the vegetated system was calculated to be $85.6 \text{ g } (\pm 3.2)$ and $63.1 \text{ g } (\pm 4.7)$ for the non-vegetated wetland (Table 3). The ($m_{\text{total}(30 \text{ min})}$) for MeP in vegetated wetlands was 29.9 g or 34.9% of the measured mass added to the system, while the $m_{\text{total}(30 \text{ min})}$ for MeP in the non-vegetated wetlands was 12.1 g or 19.2% of the measured mass (Table 3). Mass balance calculations for different sampling times indicated changes in

Table 2
Mean aqueous methyl parathion concentrations ($\mu\text{g/L}$) in wetland mesocosms during the first 10 d of exposure

Distance (m)	30 min	3 h	6 h	1 d	4 d	10 d
Vegetated						
2.5	1400	452	423	253	444	N.S.
5	717	421	298	192	22.0	4.00
10	687	184	118	90.0	14.5	0.60
20	14.0	8.15	24.9	8.00	0.60	N.D.
40	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Non-vegetated						
2.5	493	1110	615	247	72.5	3.50
5	337	552	352	185	39.0	3.00
10	54.5	121	189	164	29.5	3.50
20	4.75	44.0	72.5	35.5	22.5	0.60
40	0.15	0.30	0.55	6.00	9.00	0.55

N.S. = no sample.

N.D. = below limits of analytical detection.

Table 3

Mean methyl parathion mass (g) located in water, sediment, and plant phases of vegetated and non-vegetated wetland cells at various times throughout the study

	Mixing chamber	0.5 h	3 h	1 d	10 d
Vegetated					
Plant	—	7.84	18.4	5.22	1.58
Sediment	—	0.136	0.206	0.127	0.329
Water	—	21.9	6.42	3.22	0.027
Total	85.6	29.9	25.0	8.57	1.94
Non-vegetated					
Sediment	—	4.63	0.289	3.43	4.16
Water	—	7.48	11.0	6.18	0.13
Total	63.1	12.1	11.3	9.61	4.29

phase distribution occurring over the study duration (Table 3). Thirty minutes following the initiation of the simulated storm event, 73.3% of MeP mass in vegetated cells was in the aqueous phase, while only 26.2% of the pesticide mass was associated with plant material. Interestingly, after 3 h, the earlier mass pattern had shifted to where 73.5% of the calculated mass was present in plant material. This trend continued throughout the study, but overall mass values were decreased in the water and plant compartments after the 3 h sampling period. Throughout the study, sediment MeP mass was minimal in the vegetated wetland system with slight enrichment over time. Results from the non-vegetated wetland indicated that 30 min following the initiation of the study, 61.7% of MeP mass was in the aqueous phase. As with the vegetated wetland, a phase shift occurred over time where by 1 d the mass in water relative to sediment were relatively the same. By 10 d, the majority of the MeP mass in the non-vegetated wetland system was associated with the sediment compartment. After 10 d a total mass of 1.94 g remained (mostly associated with plants) in the vegetated wetland, while 4.29 g remained in the non-vegetated wetland. In both the vegetated and non-vegetated wetlands, less than 5% of MeP mass was associated with the water column after 10 d.

Combined changes in $m_{w(0-50)}$, $m_{s(0-50)}$ and $m_{p(0-50)}$ with time were used to estimate wetland chemical half-lives. MeP half-lives were calculated to be 2.84 and 7.80 d for the vegetated and non-vegetated wetlands, respectively, using all three compartments combined and half-lives in water were calculated to be 1.27 and 1.69 d.

3.3. Wetland length calculations

Maximum observed MeP concentrations were inversely proportional to distance downstream from the point of injection, producing regression coefficients that were significant at $p < 0.05$ (Fig. 2). Standard errors for the exponents (b) were between 0.12 and 0.59, but 95% confidence intervals spanned several orders of magnitude in terms of untransformed concentration due to the relatively small number of data points. Formulas predicted that a vegetated wetland length of 18.8 m would have been adequate to reduce MeP

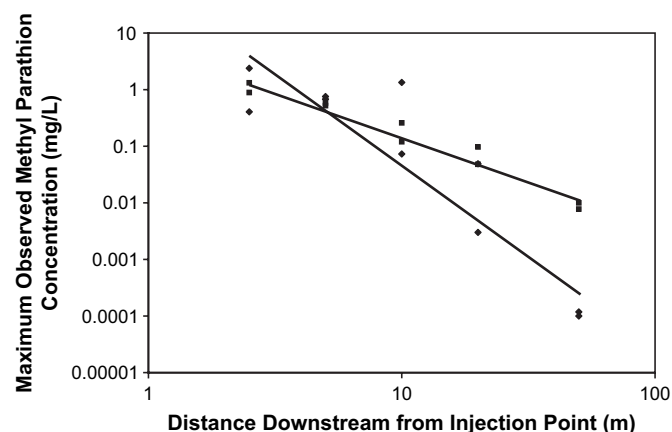


Fig. 2. Least-squares regression relationships fit to log-transformed maximum observed pesticide concentration in water collected from the vegetated wetland (◆) and the non-vegetated wetland (■) versus distance downstream from injection point. Relations are power functions of the form $y = ax^b$ where y is concentration in mg/L (vegetated wetland – $n = 10$, $a = 69.3$, $b = -3.09$, $r^2 = 0.81$; non-vegetated wetland – $n = 10$, $a = 6.1$, $b = -1.60$, $r^2 = 0.96$).

concentrations to 0.1% of the inflow concentration of 8.01 mg/L. In contrast, regression formulas indicated that a length of 62.9 m would reduce MeP concentrations to 0.1% of the inflow concentration in a non-vegetated wetland.

4. Discussion

This study was designed to evaluate the effectiveness and compare the differences of vegetated and non-vegetated wetlands on the retention and partitioning of MeP during a simulated runoff event. Results indicate the importance of a multi-compartment system that includes vegetation for efficient mitigation and degradation of methyl parathion. The concept of vegetation as a tool for contaminant mitigation is not new. Many studies have evaluated the use of wetland plants to mitigate pollutants such as acid mine drainage, metals, dairy wastes, and even municipal wastes. According to Luckeydoo et al. (2002), the vital role of vegetation in processing water passing through wetlands is accomplished through biomass nutrient storage, sedimentation, and providing unique microhabitats for beneficial microbial organisms. Macrophytes serve as filters by allowing contaminants to flow into plants and stems, after being sorbed to macrophyte biofilms (Kadlec and Knight, 1996). According to Zablotowicz and Hoagland (1999), the capability of plants to transfer contaminants from environmental matrices depends upon several factors including contaminant chemistry, plant tolerance to the contaminant, and sediment surrounding the plant (e.g. pH, redox, clay content).

Recent studies have shown the importance of aquatic vegetation for mitigation of pesticides inflow through wetlands and agricultural drainage ditches (Bennett et al., 2005; Moore et al., 2001; Schulz et al., 2003a,b). The current study has shown that aquatic vegetation plays an important role for pesticide mitigation and retention in constructed detention wetlands. The wetlands used in this study differ from that of a flow through wetland, as in Schulz et al. (2003c), by allowing only the displaced

volume to exit the wetland cell. For this type of wetland system, standpipes are used to control the wetland volume. Thus, during a runoff event wetland water is replaced/displaced until the inflowing volume has stopped. Data from this study illustrated that vegetated wetlands were capable of retaining the pulse of MeP introduced into the system during the 30 min simulated runoff. Throughout the study, MeP was not detected in water at the 40 m sampling site of the vegetated wetlands, whereas the pesticide was detected at all sites in the non-vegetated wetlands throughout the 10 d study (Table 2).

To further understand the fate of MeP in the vegetated versus the non-vegetated wetlands, mass balance calculations were performed to estimate the partitioning between the water, plant and sediment compartments. Results from the mass balance model used in this study accounted for only 34.9 and 19.2% of the MeP added to the vegetated and non-vegetated wetland systems, respectively. In an earlier study where pyrethroids were applied to a vegetated agricultural drainage ditch, the same mass balance model was utilized and pesticide recoveries were much greater (Bennett et al., 2005). It is expected that MeP mass was underestimated in this study because samples were not taken at the inlet of the wetland (point where MeP water/sediment mixture was added to the wetland systems) as in the above ditch study, and sampling was initiated at 30 min instead of time zero (as in ditch study). Owing to this, it is possible that MeP mass may have been underestimated at the front end of the system. Furthermore, MeP was detected at the outflow of the non-vegetated wetland at the 30 min sampling period indicating loss by advection from the system. Due to the high air and water temperatures (Table 1), sunny and windy conditions (personal observations) during the study's first day, other factors for MeP loss from the system may include volatilization, photodegradation, hydrolysis and biotransformation. These abiotic and biotic processes will be discussed in the following section. Regardless of the low recovery, data produced from the mass balance calculations still reveal important information on the fate of MeP in the two wetland systems.

Mass balance data indicated that both the vegetated and non-vegetated wetlands were effective in reducing the aqueous loadings of MeP introduced into each of the systems. After 10 d the majority of pesticide mass in the vegetated wetland was found in the plant compartment while the majority of pesticide was located in the sediment compartment in the non-vegetated wetland. It would be expected that sediments would play a defined role in the wetland systems since MeP has a moderately high K_{oc} (5.1×10^3) (USDA ARS, 2005). Mass balance data from this study indicate that MeP mass in sediments stabilized over time in both wetland systems, but levels were an order of magnitude higher in the non-vegetated wetland (Table 3). These data illustrate that sediment partitioning was a major process for the loss of MeP from the non-vegetated wetland system. Similarly, Crossland et al. (1986) showed that sediments were a sink for MeP in the aquatic environment and that sorption of MeP onto sediment was one of the dominant processes for loss from the water compartment. This process did not occur to the same extent in the vegetated wetland

due to the dense plant community which limited the movement and/or partitioning of MeP to the sediment compartment. Similar results were found in a microcosm study by Hand et al. (2001) where aquatic plants significantly reduced the amount of insecticide reaching the sediment. By limiting the movement into the sediment (sink), the plant compartment played an important role in the overall reduction of MeP in the system. By 10 d, the retained MeP in the vegetated wetland was less than half of the retained mass in the non-vegetated wetland even though the measured mass introduced into the system (85.6 ± 3.2 g) was greater than what was introduced into the non-vegetated wetland (63.1 ± 4.7 g; Table 3). This reduction/degradation in the vegetated wetland may have been due to many abiotic and biotic processes.

Studies have reported that the degradation of MeP occurs more rapidly in alkaline conditions relative to neutral or acidic conditions (Badawy and El-Dib, 1984; Kaur et al., 1997; Lartigues and Garrigues, 1995; USEPA, 1978). In systems rich with aquatic plants and algae, pH has been shown to exceed 9 at the water algal/plant interface as a result of photosynthetic activity (Kersting and van den Brink, 1997; Prins et al., 1980). Furthermore, *Anabaena* sp., a blue-green algal species, was able to degrade MeP under aerobic, photosynthetic conditions (Barton et al., 2004) while other studies have indicated that green and blue-green algae presence accelerate the photoreaction of MeP (Zepp and Scholtzhauer, 1983). These dense aquatic plant systems are generally laden with aufwuchs that

Table 4

Mean methyl parathion concentrations in water samples ($\mu\text{g/L}$) collected at each sampling site during the 3 h, 24 h and 96 h sampling periods relative to acute (aqueous) toxicity survival results from vegetated and non-vegetated wetland mesocosms

Site (m)	Vegetated			Non-vegetated		
	3 h	24 h	96 h	3 h	24 h	96 h
Methyl parathion ($\mu\text{g/L}$)						
5	421	192	22.0	551	184	39.0
10	184	90.0	14.5	120	164	29.5
20	8.15	8.00	0.60	44.0	35.5	22.5
40	N.D.	N.D.	N.D.	0.30	6.00	9.00
<i>Ceriodaphnia dubia</i> (%survival) ^a						
5	0	0	0	0	0	0
10	0	0	0	0	0	0
20	0	0	100	0	0	0
40	75	100	100	100	0	0
<i>Hyalella azteca</i> (%survival) ^b						
5	0	0	23	0	0	1.7
10	1.7	5.0	28	0	0	10
20	30	37	92	3.3	1.7	20
40	97	87	98	92	62	32
<i>Chironomus tentans</i> (%survival) ^c						
5	5.0	0	N.A.	3.0	0	N.A.
10	53	28	N.A.	43	0	N.A.
20	95	80	N.A.	58	28	N.A.
40	100	100	N.A.	98	93	N.A.

N.A. = data not available.

^a Milam et al. (2004).

^b Schulz et al. (2003a,b).

^c Schulz et al. (2003c).

contain bacteria that rapidly degrade MeP (Crossland and Bennett, 1984; Holm et al., 1983). Other factors such as increased water temperature (Kaur et al., 1997) (Table 1) and photolysis have also caused degradation of MeP (USEPA, 1978).

Overall, these data illustrate the importance of the plant compartment in wetland system for the mitigation of MeP. The presence of vegetation increased the rate of partitioning of MeP out of the water phase, as indicated by the shorter travel distance and failure of MeP to reach the outflow of the vegetated wetlands. Vegetated wetland effectiveness can be further illustrated by the fact that MeP was not detected in SPMDs deployed at the wetland outflow and that data from acute toxicity testing conducted in parallel with this study reflect the concentration and mass balance data (Table 4). Secondly, vegetation increased the overall rate of MeP loss out of the wetland via dissipation and/or reaction processes. Data from this study demonstrate that MeP would degrade at a slower rate in the sediment than in the water and plant compartments. There were no recorded rain events during the first 10 d of the study; however, if an event had occurred during or after the initial 10 d, it is projected that the vegetated wetland would continue to efficiently mitigate any pesticide which may be resuspended. Conversely, a lack of mitigation would likely occur in the non-vegetated wetland, due to resuspension and potential transport from the wetland system.

5. Conclusions

The presence of vegetation in stormwater treatment areas has both positive and negative effects. From an observational standpoint, excessive vegetation may slow down drainage. While this may be seen as a negative impact by some, others would view it as a positive effect, allowing increased contact time for contaminant binding to plant organic material. In fact, vegetation is often ignored in contaminant fate and effects modeling for several reasons (Cousins and Mackay, 2001). Kinetics are not well defined, because of the lack of data from vegetation uptake experiments. Vegetation is sometimes thought to contribute little to the mitigation process as compared to sediment or other matrices. However, this research reaffirms the importance of vegetation in the mitigation of pesticide-associated runoff. If contaminants (e.g. pesticides) can be bound or retained by wetland or ditch vegetation, then they will have less impact upon downstream aquatic systems.

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References

- Anderson, D.P., Zeeman, M.G., 1995. Immunotoxicology in fish. In: Rand, G.M. (Ed.), *Fundamentals of Aquatic Toxicology: Effects, Environmental Fate, and Risk Assessment*, second ed. Taylor and Francis Publishers, Washington, DC, pp. 371–404.
- Badawy, M.I., El-Dib, M.A., 1984. Persistence and fate of methyl parathion in sea water. *Bull. Environ. Contam. Toxicol.* 33, 40–49.
- Barton, J.W., Kuritz, T., O'Connor, L.E., Ma, C.Y., Maskarinec, M.P., Davison, B.H., 2004. Reductive transformation of methyl parathion by the cyanobacterium *Anabaena* sp. strain PCC7120. *Appl. Microbiol. Biotechnol.* 65, 330–335.
- Bennett, E.R., Metcalfe, T.L., Metcalfe, C.D., 1996. Semi-permeable membrane devices (SPMDs) for monitoring organic contaminants in the Otonabee River, Ontario. *Chemosphere* 33, 363–375.
- Bennett, E.R., Moore, M.T., Cooper, C.M., Smith Jr., S., 2000. Method for the simultaneous extraction and analysis of two current use pesticides, atrazine and lambda-cyhalothrin in sediment and aquatic plants. *Bull. Environ. Contam. Toxicol.* 64, 825–833.
- Bennett, E.R., Moore, M.T., Cooper, C.M., Smith Jr., S., Shields Jr., F.D., Drouillard, K.G., Schulz, R., 2005. Vegetated agricultural drainage ditches for the mitigation of pyrethroid associated runoff. *Environ. Toxicol. Chem.* 24, 2121–2127.
- Coupe, R.H., Manning, M.A., Foreman, W.T., Goolsby, D.A., Majewski, M.S., 2000. Occurrence of pesticides in rain and air in urban and agricultural areas of Mississippi, April–September 1995. *Sci. Total Environ.* 248, 227–240.
- Cousins, I.T., Mackay, D., 2001. Strategies for including vegetation compartments in multimedia models. *Chemosphere* 44, 643–654.
- Crossland, N.O., Bennett, D., 1984. Fate and biological effects of methyl parathion in outdoor ponds and laboratory aquaria. I. Fate. *Ecotoxicol. Environ. Saf.* 8, 471–481.
- Crossland, N.O., Bennett, D., Wolf, C.J.M., Swannell, R.P.J., 1986. Evaluation of models used to assess the fate of chemicals in aquatic systems. *Pestic. Sci.* 17, 297–304.
- Foreman, W.T., Majewski, M.S., Goolsby, D.A., Wiebe, F.W., Coupe, R.H., 2000. Pesticides in the atmosphere of the Mississippi River Valley, Part II – air. *Sci. Total Environ.* 248, 213–226.
- Hand, L.H., Kuet, S.F., Lane, M.C.G., Maund, S.J., Warinton, J.S., Hill, I.R., 2001. Influences of aquatic plants on the fate of the pyrethroid insecticide lambda-cyhalothrin in aquatic environments. *Environ. Toxicol. Chem.* 20, 1740–1745.
- Holm, H.W., Kollig, H.P., Payne Jr., W.R., 1983. Fate of methyl parathion in aquatic channel microcosms. *Environ. Toxicol. Chem.* 2, 169–176.
- Kadlec, R.H., Knight, R.L., 1996. *Treatment Wetlands*. Lewis Publishers, Boca Raton, FL, 893 pp.
- Kaur, I., Mathur, R.P., Tandon, S.N., 1997. Parameters affecting the decay of some organophosphorus pesticides: a study by high-performance liquid chromatography. *Biomed. Chromatogr.* 11, 22–24.
- Kersting, K., van den Brink, P.J., 1997. Effects of the insecticide Dursban 4E (active ingredient of chlorpyrifos) in outdoor experimental ditches: response of ecosystem metabolism. *Environ. Toxicol. Chem.* 16, 251–259.
- Lartigue, S.B., Garrigues, P.P., 1995. Degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions. *Environ. Sci. Technol.* 29, 1246–1254.
- Luckeydoo, L.M., Fausey, N.R., Brown, L.C., Davis, C.B., 2002. Early development of vascular vegetation of constructed wetlands in northwest Ohio receiving agricultural waters. *Agric. Ecosys. Environ.* 88, 89–94.
- Majewski, M.S., Foreman, W.T., Goolsby, D.A., 2000. Pesticides in the atmosphere of the Mississippi River Valley, Part I – rain. *Sci. Total Environ.* 248, 201–212.
- Milam, C.D., Bouldin, J.L., Farris, J.L., Schulz, R., Moore, M.T., Bennett, E.R., Cooper, C.M., Smith Jr., S., 2004. Evaluating acute toxicity of methyl parathion application in constructed wetland mesocosms. *Environ. Toxicol.* 19, 471–479.
- Mitsch, W.J., Gosselink, J.G., 1993. *Wetlands*. VanNostrand Reinhold, New York, NY, 722 pp.
- Moore, M.T., Bennett, E.R., Cooper, C.M., Smith Jr., S., Shields Jr., F.D., Milam, C.D., Farris, J.L., 2001. Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. *Agric. Ecosys. Environ.* 87, 309–314.
- National Agricultural Statistics Service (NASS), 2005. <<http://www.nass.usda.gov>>.

- Prins, H.B.A., Snell, J.F.H., Helder, R.J., Zanstra, P.E., 1980. Photosynthetic HCO_3^- utilization and OH^- excretion in aquatic angiosperms. *Plant Physiol.* 66, 818–822.
- Rice, P.J., Drewes, C.D., Klubertanz, T.M., Bradbury, S.P., Coats, J.R., 1997. Acute toxicity and behavioral effects of chlorpyrifos, permethrin, phenol, strychnine, and 2,4-dinitrophenol to 30-day-old Japanese medaka (*Oryzias latipes*). *Environ. Toxicol. Chem.* 16, 696–704.
- Schulz, R., Moore, M.T., Bennett, E.R., Farris, J.L., Smith Jr., S., Cooper, C.M., 2003a. Methyl-parathion toxicity in vegetated and unvegetated wetland mesocosms. *Environ. Toxicol. Chem.* 22, 1262–1268.
- Schulz, R., Moore, M.T., Bennett, E.R., Milam, C.D., Bouldin, J.L., Farris, J.L., Smith Jr., S., Cooper, C.M., 2003b. Acute toxicity of methyl-parathion in wetland mesocosms: assessing the influence of aquatic plants using laboratory testing with *Hyalella azteca*. *Arch. Environ. Contam. Toxicol.* 45, 331–336.
- Schulz, R., Hahn, C., Bennett, E.R., Dabrowski, J.M., Thiere, G., Day, J.A., Peall, S.K., 2003c. Fate and effects of aqueous-phase azinphos-methyl in a flow-through wetland in South Africa. *Environ. Sci. Technol.* 37, 2139–2144.
- Sokal, R., Rohlf, F.J., 1981. *Biometry*, second ed. W.H. Freeman and Company, New York, NY.
- USDA ARS, 2005. <<http://www.arsusda.gov/acsl/services/ppdb/ppdb3.html>>.
- USDA NRCS, 2002. <<http://www.nrcs.usda.gov>>.
- USEPA, 1978. Environmental pathways of selected chemicals in freshwater systems: Part II. Laboratory studies. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, GA. EPA-600/7-78/074.
- Zablutowicz, R.M., Hoagland, R.E., 1999. Microbiological considerations in phytoremediation strategies for pesticide-contaminated soils and waters. In: Rajak, R.C. (Ed.), *Microbial Biotechnology for Sustainable Development and Productivity*. Scientific Publishers (India), Jodhpur, pp. 343–360.
- Zepp, R.G., Scholtzhauer, P.F., 1983. Influence of algae on photolysis rates of chemicals in water. *Environ. Sci. Technol.* 17, 462–468.